DRAFT 10/10/2000

2.5 Ozone Carryover and Day-of-Week Phenomena Based on Data from Ozonesondes and the ARCO Tower During SCOS97

2.5.1 Abstract

Does ozone carryover aloft affect day-of-the-week phenomena? Given substantially limited and intermittent data aloft that are currently available, both in time and in space, we cannot resolve this question. Nevertheless, the work reported here suggests a better question - how does carryover of ozone and aged pollutants aloft affect day-of-the-week ground level ozone phenomena. This limited analysis suggests that carryover of ozone does have day-of-the-week influences. Without the routine effect of carryover, ground level ozone concentrations are usually reduced on Mondays. Polluted air in layers aloft can routinely affect ground level ozone concentrations. As indicated by the analyses below, some polluted layers are at least 2 days old and can routinely impact ozone concentrations at ground level. On one occasion, the contribution of ozone concentrations aloft to ozone concentrations at ground level was 20 parts per billion volume (ppbV), or 30 percent of the ozone loading at ground level.

2.5.2 Introduction

Until the latter half of the 1990s, Saturday was the day-of-the-week with the highest peak concentration of ambient ozone in the South Coast Air Basin (SoCAB) [*Austin & Tran*, 1999; *Winer & Blier*, 1999; *Winer & Blier*, 1996]. Sunday now appears to have replaced Saturday as the day-of-the-week with the highest peak concentration of ambient ozone in the SoCAB (*Austin & Tran*, 1999; *Winer & Blier*, 1999). Various potential factors contributing to the Ozone Weekend Effect have been hypothesized. One hypothesis is that carryover of ozone and other pollutants aloft affect or influence ozone photochemistry at ground level. For this mechanism to be a contributor to the Weekend Effect, carryover of ozone aloft needs to occur routinely and the pollution aloft must be sufficiently low in altitude to be "tapped" by the increased vertical mixing of the atmosphere during the morning and early afternoon. This analysis examines data collected from a tall building and with ozonesondes during the 1997 Southern California Ozone Study (SCOS97) to address the potential for carryover aloft.

2.5.3 Methodology

During SCOS97, ARB staff operated a Dasibi 1003-AH ultraviolet photometry ozone analyzer at the Atlantic Richfield Company (ARCO) headquarter tower (100 meters above ground level (agl); 198 meters above mean sea level (msl)) in central Los Angeles. On July 18, 1997, an ARB audit team invalidated these data because the temperature of the analyzer compartment was not recorded, the data logger was inoperative, and the inlet was not at least one (1) meter away from the building. For these reasons, the data did not meet federal Environmental Protection Agency (EPA) guidelines. In addition, the analyzer output deviated 8% high from the true value. Based on previous experiences, most data analysts believe these ozone analyzers do not produce erroneous data due to high room temperature and have confidence in the ozone data from ARCO tower.

The South Coast Air Quality Management District operates a routine monitoring site located inside a Los Angeles Department of Water and Power facility on North Main Street (LANM). The ARCO tower is roughly one mile west-south-west of LANM. The data from these two sites provide a rough but continuous idea of the lowest portion of the atmosphere and low ozone layers aloft. The LANM data met the federal EPA quality guidelines.

During SCOS97, ozonesondes (balloons with potassium iodine total oxidant instruments, and temperature and relative humidity capacitance probes) were launched from seven locations. The University of Southern California's (USC) Hancock Foundation Building, located south of Central Los Angeles, was one of the ozonesonde release sites. Balloons were launched at 0200, 0800, 1400, and 2000 Pacific Daylight Time (PDT). The USC site is located 4 miles southwest of LANM. The USC data provide a snapshot-in-time view of the vertical profile of ozone concentrations and meteorological conditions aloft. The USC ozone balloon data have passed "level 1" quality guidelines [*Fujita* et. al., 1999].

2.5.4 Results & Discussion

2.5.4.1 ARCO Tower

Ozone concentrations at the ARCO tower and LANM averaged 29.6 and 29.5 ppb, respectively, for the period of this analysis. On average, the difference between concentrations at ARCO tower and LANM (ARCO-LANM) was 10 ppbV but the 75th percentile values were significantly above the average and the 25th percentile values were negative. These differences were not merely due to differences in measuring instruments (the 8% bias was removed). Positive values are indicative of ozone aloft or ozone titration near ground level. Values near zero are indicative of good atmospheric mixing and movement of ozone layers downwards. Negative values are indicative of ozone aloft having been tapped or transported downwind. On average, there were higher ozone concentrations even less than 100 meters above ground level (agl) than at ground level (Figure 2.5-1).

Looking at these differences on a coupled, day-to-day basis, correlation between these differences suggests that the Friday to Saturday and Sunday to Monday transitions occur very differently than other day-to-day transitions (Table 2.5-1). Accepting that ozone mixes downwards affecting ground level concentrations during most days of the week, Monday and Saturday ground level ozone concentrations benefit differently from carryover because the relationship between ground level and aloft ozone seems to be stronger (Table 2.5-1). Based on the foregoing, interaction of ozone aloft (100 meters) with ground level concentrations exhibits a day-of-the-week effect. To further investigate this potential influence at ARCO and LANM during

SCOS97, we reviewed how hourly ozone concentrations from one day are related to ozone concentrations on the following day. These tables for ARCO and for LANM suggest a strong relationship between the diurnal profile of hourly ozone concentrations on one day and on the next day. However, differences in ozone concentrations (ARCO minus LANM) for each hour from one day to the next day, on a daily basis rather than on a seasonal basis (Table 2.5-2), offer a different perspective.

When there were significant differences in the vertical profile of ozone concentrations (lightly shaded squares in Table 2.5-2; R^2=0.01 to 0.03), such changes occurred most frequently with Fri-Sat (2), Sat-Sun (1), Sun-Mon (1), and Wed-Th (1) pairs. We noted previously that Sunday to Monday and Friday to Saturday showed changes in ozone aloft different from other days (Table 2.5-1). Otherwise, there was significant continuity or persistence (darkly shaded squares in Table 2.5-2; R^2=0.8 to 0.9) of ozone profiles aloft spread throughout the days of the week Th-Fri (1), Sat-Sun (1), Sun-Mon (2), Mon-Tue (3), Tue-Wed (2), Wed-Th (1). This is analogous to saying the weather tomorrow is likely to be similar to today's weather. Carryover generally depends on continuation of ozone aloft to build stronger aloft layers. Significant correlation changes may signal removal/dispersion or formation/advection of aloft layers. The build-up of stronger aloft layers seemed not to vary by day-of-the-week. This may have to do with emissions being constant throughout the week and the build-up of stronger aloft layers being governed by meteorology. However, removal/exhaustion of ozone layers aloft varied strongly by day-of-the-week. This may have to do with ozone aloft layers mixing down and being used up in titration and removal at ground level much more strongly on Mondays because the ozone layer close to ground has been thoroughly used up during the weekend.

To explore the magnitude of the day-to-day changes, we assembled daily maximum-hour concentrations for the LANM site during SCOS97. Consistent with the Ozone Weekend Effect, Sunday was the highest ambient ozone day of the week at the LANM site during SCOS97. We have noted occasions with high ozone concentrations (>80 ppbV) in red followed by low concentrations (#60 ppbV in blue) in Table 2.5-3. Such changes are rare (5) and occur Sunday to Monday (3) and Tuesday to Wednesday (2). The most extreme of these day-to-day changes (>50 ppbV- underlined) coincide with very low correlation between day-to-day ozone aloft profiles (0.01, 0.23, and 0.13 R^2 in order of appearance in Table 2.5-3). We hypothesize that exhaustion of ozone layers aloft is expressed in weak day-to-day ozone aloft correlation, and coincided with extreme changes in day-to-day ozone. Two out of three such occasions occurred Sunday to Monday.

To examine how day-to-day changes in ground level ozone and in ozone layers aloft may be related, Table 2.5-2 is referenced again but we shaded the day-to-day couples with ground level ozone concentration reductions of 30 ppbV or more (Table 2.5-4). Such reductions occurred from Sunday to Monday (5), Monday to Tuesday (1), Tuesday to Wednesday (1), and Wednesday to Thursday (1). No such reduction occurred between Thursday and Sunday. Sunday to Monday correlations were either high (R^2 = 0.8 or higher) or low (0.13 or 0.01). Other days of the week had moderate correlations (R^2 of 0.52, 0.61, and 0.63).

The high R^2 correlations for Sunday to Monday differences may indicate that ozone layers aloft did not significantly alter ground level concentrations and Monday's fresh nitrogen oxide emissions significantly reduced ground level ozone concentrations. The low R^2 may indicate a total exhaustion of aloft profiles as they existed the day before. Both phenomena indicate that whenever ozone concentrations decrease significantly on Mondays, carryover aloft is not effective in assisting ground level photochemistry.

Because increases of ground level ozone from day to day was of interest, we present Table 2.5-2 with shaded cells denoting 20 ppbV or more increases of LANM ozone from day to day (Table 2.5-5). Such increases occurred from Thursday to Friday (2), Friday to Saturday (2), Saturday to Sunday (4), and Tuesday to Wednesday (1). R^2 values vary widely (0.14 to 0.85) but they are never very low (0.01 to 0.03). Decreases in ground level ozone concentrations showed influence of carryover manifested in either ozone aloft profiles not changing at all from day to day or changing significantly. Carryover seen in strong or weak correlation between ozone aloft profiles had a day of the week influence. Moreover, ground level ozone concentrations declined more significantly in the absence of contribution from ozone aloft. There were indications that ozone aloft profiles had a day-of-week relationship and that the absence of carryover was related to significant reductions in ground level ozone concentrations. The remaining issue was to demonstrate that carryover processes could take place during two or more days of atmospheric chemistry.

2.5.4.2 Ozonesondes

So far we have only presented implications of analyses of the data collected from the first 100 meters of the ozone vertical profile at a source site during SCOS97. Continuous aloft data at more sites and for a more significant fraction of the aloft profile would provide a better understanding of carryover. During SCOS97, ozone data collected with a balloon provided a snap shot of the entirety of the aloft profile. Looking at these snapshots in view of the evolution of ground level concentrations provided another piece of anecdotal analysis to focus on multi-day carryover events.

It is conceptually convenient to separate the closest layer to the ground (up to 500 to 700 meters agl) as the compartment in the atmosphere most susceptible to interaction with the ground-based emissions and atmospheric chemistry associated with these emissions. Due to the cessation of photochemical production of ozone, the influence of the nocturnal boundary conditions, and the nighttime emissions of nitrogen oxide, ozone concentrations in this reservoir layer may be reduced to very low concentrations nocturnally. During the day, much of ozone buildup related to that day's atmospheric chemistry fills this compartment first. For further convenience we have called this layer the Reservoir (Figure 2.5-3).

There are a series of layers of ozone above the reservoir (from 500-700 up to 3,000-4,000 meters agl) that can be viewed for conceptual convenience as one alpha layer. These layers are influenced by flow of ozone from the reservoir (daytime) and from above the alpha layer and in turn can influence ozone in the reservoir. Ozone concentrations are not significantly reduced at night because nighttime ground deposition and nitrogen oxide emissions have no significant impact on these layers. Thus, the alpha layer may exist at high concentrations for several days. Although their interaction with the reservoir and their consequent impact on ground level ozone concentrations depend entirely on the meteorological factors, the ozone concentration load they contain depends entirely on reservoir ozone formation processes that occurred one or several days before.

There are yet a third series of ozone layers above the alpha layer (from 3,000-4,000 up to 6,000+ meters agl) that can be viewed for conceptual convenience as one beta layer. These layers can be influenced by flow of ozone from the alpha and reservoir layers and in turn may influence the alpha and reservoir layers, more importantly they have a regional nature and speak more to the background ozone concentrations. It is important to keep in mind the three-dimensional nature of ozone layers aloft in the complex southern California Bight where land-sea interactions play a critical role in developing regional meteorology and atmospheric chemistry. Designation of these layers is only for convenience and cannot reflect the full complexity of ozone aloft phenomena.

Nevertheless, a series of USC balloon snapshots of the ozone vertical profile is indicative of interaction of the alpha layers with ground levels. In particular, these interactions are noted for the August 22nd to 23rd high ozone episode (Friday to Saturday). By the early morning hours (0200) before Saturday, August 23rd, the alpha layer had perhaps 60 to 80 ppbV of ozone within it while the reservoir was essentially exhausted. While the reservoir grew by atmospheric chemistry of morning emissions (0800 hours snapshot), boundary conditions improved to permit more mixing and by 1400 hours the alpha layer seemed to have mixed with the reservoir. There were indications that carryover affected the ground level concentrations (Figure 2.5-4 through Figure 2.5-8).

The USC snapshots from September 4 (Thursday) to 6 (Saturday) indicate that such carryover can take place over more than one day. A narrow alpha layer containing roughly 80 ppbV of ozone began on Thursday and was reinforced during Thursday, existed during Friday and weakened somewhat but did not mix down, and finally mixed down on Saturday and was entirely exhausted contributing to a peak of 66 ppbV at LANM. Carryover from Thursday affected Saturday's ground level ozone concentrations (Figure 2.5-9 through Figure 2.5-14).

The limited analyses presented here do not account for the fact that photochemical processes aloft are rather like ground level processes in that ozone, reactive organic gases, and nitrogen species are part of a complex set of chemical interactions that continue away from emission sources. These limited analyses are two-dimensional snap shots of a three-dimensional phenomena that encompasses the entirety of the southern California Bight and includes land-sea interactions and air parcel transport processes. Furthermore, the implications of the analyses may be limited because the meteorological conditions during the summer of 1997 were not typical of normal summer conditions due to a strong El NiZo. Nevertheless, there is evidence that ozone in layers aloft affected ground level concentrations and that such carryover aloft can persist more than one day.

2.5.5 Conclusions

There are indications that for a source area during SCOS97, carryover of ozone aloft had day-of-the-week influences and that, without the effect of carryover aloft, ground level ozone concentrations would be less than otherwise. There are also indications that layers of ozone aloft, some at least 2 days old, affected ground level concentrations.

2.5.6 Recommendations

This type of analysis is critical to evaluate regional air pollution transport assessment. With the expansion of transport assessment to trans-national air pollution transport (to and from Mexico and to and from People's Republic of China), these analyses are even more relevant and important for California. Continuous ozone aloft measurements using light detection and ranging during several ozone seasons would provide a database to properly conduct this critical analysis. Continuous measurements of aged hydrocarbons during several ozone seasons using tethered balloons offshore and in the Mojave Desert and Salton Sea air basins would also help this type of critical analysis.

2.5.7 References

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Blier, W., and A. Winer (1999) "Analysis of Weekday/Weekend Differences in Ambient Air Quality and Meteorology in the South Coast Air Basin," Air Resources Board Contract No. 95-334, June.

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Table 2.5-1. Correlations (R^2) of Day-Pair Ozone Concentration Differences at and between ARCO and LANM during SCOS97

Day-Pair	Difference between ARCO & LANM Difference	Difference at ARCO	Difference at LANM
	Correlation Coefficient		
THURSDAY-FRIDAY	**0.67**	**0.74**	**0.80**
FRIDAY-SATURDAY	***0.49***	***0.69***	**0.81**
SATURDAY-SUNDAY	**0.73**	**0.82**	**0.87**
SUNDAY-MONDAY	***0.58***	***0.68***	**0.83**
MONDAY-TUESDAY	**0.79**	**0.70**	**0.81**
TUESDAY-WEDNESDAY	**0.55**	**0.63**	**0.64**
WEDNESDAY-THURSDAY	**0.53**	**0.66**	**0.78**

Table 2.5-2. Correlation of Hourly ARCO-LANM Differences for Individual Day-to-Day Pairs during SCOS97

	R^2 for Relationship between Daily ARCO-LANM Differences						
Week	Th-Fri	Fri-Sat	Sat-Sun	Sun-Mon	Mon-Tue	Tue-Wed	Wed-Th
3-Jul		**0.29**	**0.18**	**0.01**	**0.26**	**0.84**	**0.35**
10-Jul	**0.34**	**0.14**	**0.31**	**0.14**	**0.48**	**0.17**	**0.30**
17-Jul	**0.23**	**0.39**	**0.01**	**0.36**	**0.07**	**0.30**	**0.67**
24-Jul	**0.12**	**0.09**	**0.14**	**0.10**	**0.68**	**0.09**	**0.52**
31-Jul	**0.68**	**0.32**	**0.45**	**0.39**	**0.68**	**0.52**	**0.14**
7-Aug	**0.28**	**0.48**	**0.27**	**0.43**	**0.71**	**0.35**	**0.03**
14-Aug	**0.22**	**0.01**	**0.14**			**0.60**	**0.60**
21-Aug					**0.78**	**0.75**	**0.60**
28-Aug	**0.66**	**0.67**	**0.64**	**0.91**	**0.85**	**0.66**	**0.79**
4-Sep	**0.81**	**0.58**	**0.56**	**0.33**	**0.57**	**0.51**	**0.56**
11-Sep	**0.59**	**0.40**	**0.62**	**0.86**	**0.38**	**0.90**	**0.44**
18-Sep	**0.71**	**0.43**	**0.85**	**0.78**	**0.63**	**0.23**	**0.52**
25-Sep		**0.51**	**0.65**	**0.13**	**0.86**	**0.74**	**0.61**
2-Oct	**0.40**	**0.32**	**0.10**	**0.69**	**0.89**	**0.79**	**0.13**
9-Oct	**0.50**	**0.18**	**0.31**	**0.60**	**0.48**	**0.73**	**0.85**
16-Oct		**0.01**	**0.31**				

Table 2.5-3. Daily maximum- hour ozone concentrations at Los Angeles – N. Main

LANM Peak Ozone Concentration (ppb)							
Week	**Fri**	**Sat**	**Sun**	**Mon**	**Tue**	**Wed**	**Th**
3-Jul	102	87	98	46	45	46	48
10-Jul	35	37	56	44	40	44	60
17-Jul	43	39	46	51	22	56	40
24-Jul	50	46	57	49	41	55	58
31-Jul	61	85	96	82	90	59	52
7-Aug	46	38	34	34	40	54	61
14-Aug	46	37	59		17	33	43
21-Aug	56	80	87	45	59	70	62
28-Aug	60	86	120	86	73	68	73
4-Sep	36	66	64	56	61	58	33
11-Sep	41	56	75	42	32	35	59
18-Sep	29	38	73	81	82	31	35
25-Sep	36	83	111	60	66	68	28
2-Oct	47	59	59	36	31	43	35
9-Oct	30	33	36	40	23	26	
16-Oct	53	56	57				

Table 2.5-4. Correlation of Hourly ARCO-LANM Differences for Day-to-Day Pairs

R^2 for Relationship between Daily ARCO-LANM Differences

Day to Day Increases of 30 ppbV or More*

Week	Th-Fri	Fri-Sat	Sat-Sun	Sun-Mon	Mon-Tue	Tue-Wed	Wed-Th
3-Jul		0.29	0.18	0.01	0.26	0.84	0.35
10-Jul	0.34	0.14	0.31	0.14	0.48	0.17	0.30
17-Jul	0.23	0.39	0.01	0.36	0.07	0.30	0.67
24-Jul	0.12	0.09	0.14	0.10	0.68	0.09	0.52
31-Jul	0.68	0.32	0.45	0.39	0.68	0.52	0.14
7-Aug	0.28	0.48	0.27	0.43	0.71	0.35	0.03
14-Aug	0.22	0.01	0.14			0.60	0.60
21-Aug					0.78	0.75	0.60
28-Aug	0.66	0.67	0.64	0.91	0.85	0.66	0.79
4-Sep	0.81	0.58	0.56	0.33	0.57	0.51	0.56
11-Sep	0.59	0.40	0.62	0.86	0.38	0.90	0.44
18-Sep	0.71	0.43	0.85	0.78	0.63	0.23	0.52
25-Sep		0.51	0.65	0.13	0.86	0.74	0.61
2-Oct	0.40	0.32	0.10	0.69	0.89	0.79	0.13
9-Oct	0.50	0.18	0.31	0.60	0.48	0.73	0.85
16-Oct		0.01	0.31				

* Shaded Areas with 30 ppbV Day-to-Day Decrease at LANM

Table 2.5-5. Correlation of Hourly ARCO-LANM Differences for Day-to-Day Pairs

R^2 for Relationship between Daily ARCO-LANM Differences							
Day to Day Decreases of 20 ppbV or More*							
Week	**Th-Fri**	**Fri-Sat**	**Sat-Sun**	**Sun-Mon**	**Mon-Tue**	**Tue-Wed**	**Wed-Th**
3-Jul		0.29	0.18	0.01	0.26	0.84	0.35
10-Jul	0.34	0.14	0.31	0.14	0.48	0.17	0.30
17-Jul	0.23	0.39	0.01	0.36	0.07	0.30	0.67
24-Jul	0.12	0.09	0.14	0.10	0.68	0.09	0.52
31-Jul	0.68	0.32	0.45	0.39	0.68	0.52	0.14
7-Aug	0.28	0.48	0.27	0.43	0.71	0.35	0.03
14-Aug	0.22	0.01	0.14			0.60	0.60
21-Aug					0.78	0.75	0.60
28-Aug	0.66	0.67	0.64	0.91	0.85	0.66	0.79
4-Sep	0.81	0.58	0.56	0.33	0.57	0.51	0.56
11-Sep	0.59	0.40	0.62	0.86	0.38	0.90	0.44
18-Sep	0.71	0.43	0.85	0.78	0.63	0.23	0.52
25-Sep		0.51	0.65	0.13	0.86	0.74	0.61
2-Oct	0.40	0.32	0.10	0.69	0.89	0.79	0.13
9-Oct	0.50	0.18	0.31	0.60	0.48	0.73	0.85
16-Oct		0.01	0.31				

* Shaded Areas with 20 ppbV Increase Day to Day at LANM.